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Adsorbate Reorganization at Steps: NO on Pd(211)

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The interaction of nitric oxide, NO, with the stepped Pd(211) surface is studied using density functional theory slab calculations. Calculated chemisorption energies and geometries reveal that surface sites are not populated in a sequential manner as the NO coverage is increased. This comes about through mutual NO interactions that reorganize the adsorbates during the adsorption. The finding of nonsequential site population allows a reinterpretation of existing experimental data. [S0031-9007(97)04652-8]

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Most surfaces are heterogeneous in the sense that they will include different facets or steps and other defects [1]. Adsorbates and reaction intermediates may exhibit largely different stability and bonding character at various surface sites, and control of the reactivity and selectivity of a surface is closely related to the ability to design surfaces with particular structures [2].

The discussion of surface heterogeneity in adsorption often relies on the assumption of a sequential population of the various sites. In this linear model the adsorption sites with the largest bond energy are filled first, and as the chemical potential of the adsorbate is increased, sites that are less and less stable are populated [3–7]. In the present Letter we provide theoretical evidence from self-consistent density functional theory calculations that such a simple view is not always applicable. We will show that adsorbate-adsorbate interactions can be as strong as the intrinsic surface inhomogeneity so that the stability of different adsorption sites interchanges as the surface coverage is increased. In other words, the adsorbates reorganize at the surface at higher coverage due to their mutual interactions.

To illustrate our point we have studied nitric oxide (NO) adsorption on Pd(211). This surface consists of (111) terraces and (100) steps and therefore has a strong intrinsic heterogeneity. Moreover, the experimental results for this surface are very interesting. Combined ES-DIAD and HREELS experiments have shown [6,7] that at low coverages NO is adsorbed in a state with the NO axis perpendicular to the terraces and as the coverage is increased a new state, which is tilted with respect to the terrace plane, is observed. In the sequential adsorption model this is interpreted as NO adsorbed first at the terraces and then—with a smaller adsorption energy—at the steps. This makes the NO/Pd(211) system an exception to the general rule that the adsorption at steps is stronger than at terraces [3–5,8]. In this Letter we show that when adsorbate-adsorbate interactions are taken into account the anomaly disappears.

In the present Letter we use density-functional theory and adopt a slab approach towards the description of

the metallic surface. Twelve metal Pd fcc(211) layers are repeated periodically in a supercell geometry with 8.4 Å of vacuum between the slabs. The Pd-GGA lattice parameter of 3.96 Å is used. In all cases, we use a (2×1) surface unit cell, with two Pd atoms in the close-packed direction parallel to the step edge. Adsorption of NO is done on one of the two slab surfaces and the uppermost four Pd(211) layers are relaxed together with the adsorbate(s) in the search for stable sites. The ionic cores are described by pseudopotentials [9] and the Kohn-Sham one-electron valence states are expanded in a basis of plane waves with kinetic energies below 40 Ry at a uniform (4×4) sampling mesh within the first Brillouin zone [10]. NO/Pd(211) bond energies are found to change by less than 20 meV upon expansion of the basis set with plane waves up to 50 Ry while the differences between bond energies change by less than 1 meV. The exchange-correlation energy and potential are described by the GGA-II expression [11]. The bridge site adsorption of NO on (100) facets of Ni, Rh, Pd, and Pt has recently been shown by Hass *et al.* [12] to lead to a complete quenching of the magnetic moment on the NO molecule. In our work, we find similar results for both bridge and threefold bonded NO on the edge of the Pd(211) step and we therefore here report on the results of spin-restricted calculations without any loss of accuracy. The self-consistent GGA density is determined by subsequent iterative diagonalization of the Kohn-Sham Hamiltonian, Fermi population of the Kohn-Sham states ($k_B T = 0.1$ eV), and Pulay mixing of the resulting electronic density [10]. All total energies have been extrapolated to $k_B T = 0$ eV. The reported bond energies of the n th NO in the Pd(211) (2×1) cell are calculated by $E_{\text{bond},n} = -(E_{\text{tot}}^{\text{Pd},n\text{NO}} - E_{\text{tot}}^{\text{Pd}} - n \cdot E_{\text{tot}}^{\text{NO}}) - \sum_{i=1}^{n-1} E_{\text{bond},i}^{\text{opt}}$, where $E_{\text{tot}}^{\text{Pd},n\text{NO}}$ is the total energy of the fully relaxed interacting NO/Pd(211) (2×1) system with n NO molecules, $E_{\text{tot}}^{\text{Pd}}$ the total energy of the clean, fully relaxed Pd(211) surface, $E_{\text{tot}}^{\text{NO}}$ the total energy of the gas-phase, spin-polarized NO molecule, and $E_{\text{bond},i}^{\text{opt}}$ the largest bond energy found for the i th NO in the cell.

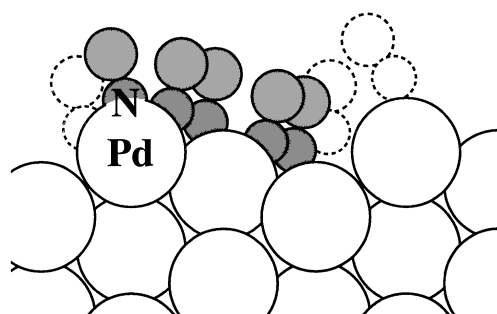
We first consider NO adsorption on the Pd(211) surface at a low NO coverage, $\theta_{\text{NO}} = 1/6$ (one NO per six Pd atoms exposed by the surface). The NO is adsorbed in a number of surface sites, the nuclear coordinates are relaxed, and for five of the starting configurations we find that the total energy exhibits a local minimum close by. These configurations are shown as sites I through V in Fig. 1. Other starting configurations were tried (some of which are shown as *a* through *c* in the figure), but did not reveal any stable configurations near by, other than the ones already found. Of the five stable configurations found, three (I through III) involve NO bound to at least one step Pd atom while the remaining have the NO bound to terrace Pd atoms only. NO is threefold coordinated with respect to the Pd atoms in most sites, the only exception being site I, where the NO is twofold coordinated. The notion of *step bound NO* will be used in the following for sites I and II as the NO in these mostly coordinate to Pd step atoms, while the NO in the remaining sites will be termed *terrace bound NO*.

The NO-Pd(211) bond energy at the various sites is given in Table I and shown in Fig. 2. Step bound NO is seen to be favored over terrace bound NO. It is also

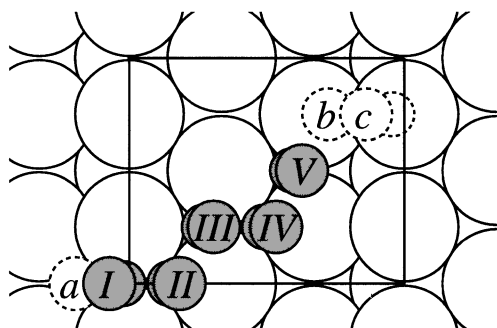
favored over adsorption of one-sixth of a monolayer of NO in the fcc threefold site on the flat Pd(111) surface for which a separate calculation gives an adsorption energy of 2.17 eV. Among the step bound NO on the Pd(211), site II is slightly preferred over site I. The terrace bound NO on Pd(211) has an adsorption energy which resembles that of NO on the flat Pd(111); however, on Pd(211) NO becomes more and more weakly bound the further into the terrace the NO is moved. We shall return to a discussion of the origin of this behavior below.

First, however, we increase the NO coverage to $\theta_{\text{NO}} = 1/3$ [two NO per Pd(211)-(2 × 1)]. To find the optimum configuration at this coverage, we start by populating one of the NO sites I or II that were found above to be the most stable ones in the low coverage limit. These species are shown by the small white circles in Fig. 3. Then a number of structural optimizations are performed from starting configurations with a second NO in the sites I–V shown by the shaded circles in the figure. Except for one system [Pd(211)-(2 × 1)-2NO-II, III] where the two NO molecules were initiated in very close proximity, local energy minima were found close by for all these starting configurations. The corresponding bond energies of the last NO added to the (2 × 1) cell are reported in Table I and Fig. 2. The second NO in the Pd(211)-(2 × 1) cell clearly prefers to become terrace bound. The configuration where the step bound NO species is in the threefold site is, however, no longer the preferred one. This implies that even for the relatively low coverage situation considered ($\theta_{\text{NO}} \sim 1/6$ – $1/3$), the adsorption of NO on an NO precovered Pd surface induces a change in the site preference of the preadsorbed NO which consequently moves from site II to I. We illustrate schematically in Fig. 4 the dynamics of this surprising result.

Before considering what the possible reasons are for the calculated site preferences and for the adsorbate reorganization, we turn to a comparison to the experimental results. At first, the exceptional experimental finding [6,7] of preferential adsorption onto the terraces for the NO/Pd(211) system mentioned above seems to be at variance with the present Letter. However, this comes about only when the experimental data is interpreted in terms of a traditional sequential site population model. In the light of our finding above that such a model is not always applicable we now revisit the experimental data [6]. The experiment was



Side view



Pd(211)-(2x1)-1NO, top view

FIG. 1. Adsorption sites, I through V, for an NO (small shaded circles) put in the Pd(211)-(2 × 1) surface cell (indicated by the rectangle). Only one site is populated at a time. Species I is pointing 17° in the downstairs direction while species II through V all are pointing more or less in the direction normal to the terrace plane; II is for instance pointing 15° in the upstairs direction. The small dotted circles, *a*, *b*, and *c*, show the NO in nonstable configurations, which are only partially relaxed.

TABLE I. The NO-Pd(211) bond energy, E_{bond} , in eV of the last NO added to the configurations shown in Figs. 1 and 3. $E_{\text{bond},1}^{\text{opt}} = 2.26$ eV is used for all $E_{\text{bond},2}$ values.

	$E_{\text{bond},1}$ (2 × 1)-1NO	$E_{\text{bond},2}$ (2 × 1)-2NO-I	$E_{\text{bond},2}$ (2 × 1)-2NO-II
I	2.23	1.28	1.67
II	2.26	1.67	1.45
III	2.17	1.78	...
IV	2.06	1.96	1.79
V	1.86	1.79	1.79

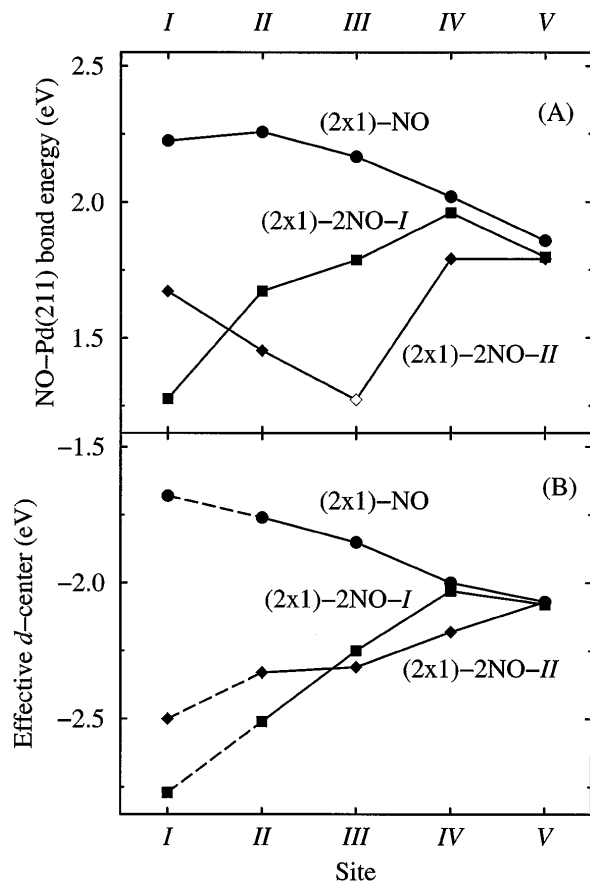
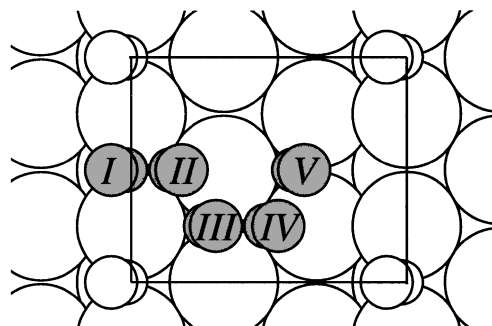
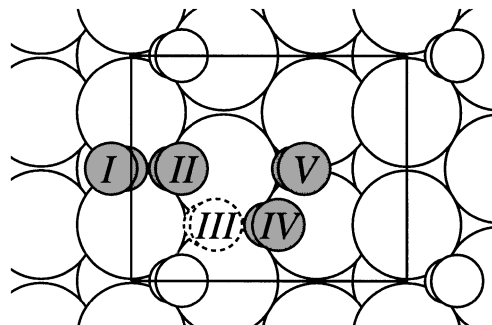


FIG. 2. (a) NO bond energies on Pd(211) (solid symbols: stable configurations; open symbols: estimates for unstable configurations; lines: guides to the eye). The sites I–V are defined in Figs. 1 and 3. (b) The effective d -band center seen by the NO at the various sites. The centers are calculated before the last NO is added—i.e., from the clean, unrelaxed Pd(211) surface and from the Pd(211)-(2 × 1)-1NO surface with the NO in sites I and II, respectively. The connections between twofold and threefold sites are only dashed.

performed at a range of NO exposures. At low NO coverage, an HREELS energy loss was found at 1535 cm^{-1} and a corresponding ESDIAD peak at $+14^\circ$ (indicative of upstairs pointing NO). At high NO coverage, HREELS energy losses were detected at around 1545 and 1655 cm^{-1} while ESDIAD features now were present at $+16^\circ$ and -16° . Now, the important step in the analysis of this data is to realize that the two small HREELS energy losses and the two ESDIAD features at positive angles do not necessarily originate from the same NO species. Our calculations reveal that at low NO coverage an upstairs pointing NO is in the step bound site II, while at high coverages another upstairs pointing NO is in the terrace bound site IV. This explains why the ESDIAD probes upstairs pointing NO at an extended range of coverages (without the assumption that these NO are absorbed in the same site). At higher NO coverages, the calculations give evidence of a downstairs pointing NO in site I in agreement with the ESDIAD results. Calculated vibrational frequencies of the adsorbed NO also support the present assignment of



Pd(211)-(2x1)-2NO-I



Pd(211)-(2x1)-2NO-II

FIG. 3. Adsorption sites, I through V, for the second NO adsorbed in the Pd(211)-(2 × 1) surface cell (shaded circles: stable sites; dotted circles: unstable sites). In the upper panel, the preadsorbed NO (small open circles) is in the twofold step bound site, I, while in the lower panel it is in the threefold step bound site, II (see Fig. 1).

the order of population and reorganization of the NO sites. While the stretch modes of NO in the two threefold sites II and IV are calculated to be 1730 and 1710 cm^{-1} , respectively, the corresponding stretch mode of the twofold step bound NO in site I is found to be 1850 cm^{-1} —i.e., about 130 cm^{-1} higher than the other two. This agrees well with the experimental HREELS data which evidences low energy losses at all coverages while a loss at approximately 115 cm^{-1} higher energy is detected only at large NO coverages [13]. The present reanalysis of the experimental

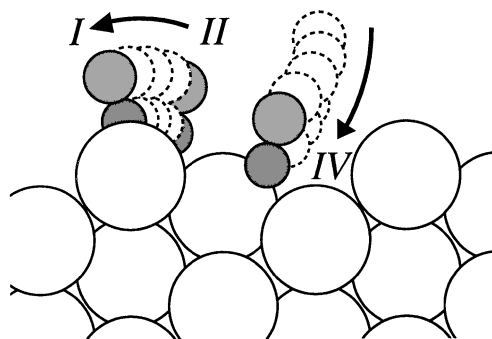


FIG. 4. Schematic illustration of the presumed pathway for the reorganization of NO at Pd(211) upon adsorption of two NO per (2 × 1) surface cell. The adsorption of NO into site IV stabilizes site I over II for the preadsorbed NO.

results shows that step bound NO species are present at both low and high coverages. It thus supports the general picture that the bonding of adsorbates at step sites is more stable than at terrace sites. But it also shows that this sometimes becomes apparent only when considering that sites may populate in a nonsequential manner due to adsorbate reorganizations.

Having established that the present theoretical results are consistent with the experimental data we turn to the question of the reasons for the order of site preference and the adsorbate reorganization during the adsorption. We suggest that the trends can be rationalized using two principles: (1) NO prefers to adsorb on threefold sites on Pd(111), and (2) all other things equal, NO prefers to adsorb at metal atoms with high lying d bands.

The first principle is a somewhat weak effect. On Pd(111) the bond energy of NO in twofold sites is 0.3 eV smaller than in the threefold sites. The second principle is evident from Fig. 2(b). For sites II–V which are all threefold sites there is an excellent correlation between the bond energy and the d -band center ϵ_d , averaged over the three Pd neighbors—the higher the d -band center, the stronger the bond. Even the adsorbate reorganization at higher coverage can be understood on this basis. First of all, it is seen in Fig. 2(b) that when NO is preadsorbed in either site I or II, sites IV and V become the ones with the highest d -band centers and hence the highest expected bonding energies. It can also be seen that the center of the d states at site IV is considerably higher when the preadsorbed NO is in site I compared to II. As the energy difference between these two sites is small in the first place, the d -band upshift at site IV provides the driving force for the adsorbate reorganization at high coverages. It is thus the ability of the substrate to bond more strongly to terrace bound NO introduced at higher coverages that drives the preadsorbed step bound NO out of its preferred threefold bonding site to the twofold bonding site. We note that the correlation between the d -band center and the calculated bond energy in Fig. 2 applies only where the NO-NO separations are sufficiently large that direct NO-NO Pauli and dipole repulsion terms can be disregarded. In fact, for very small NO-NO separations, such repulsive terms may even dominate the energetics as seen in Fig. 2 for a couple of cases—in particular for the case of simultaneous NO adsorption in sites II and III, which turns out to be unstable [the open diamond in Fig. 2(a)] apparently because the NO's are in neighboring threefold sites. Apart from such special cases, however, the d -band center ϵ_d generally seems a reasonable reactivity measure. The question is why? We suggest that the coupling between the antibonding $2\pi^*$ molecular state above the Fermi level and the d states becomes stronger as the latter moves up towards the former [14]. The degree to which the d states move in energy from one site to the next can be described in a moment expansion of the d density of states, the first term of which is the center, ϵ_d .

The variation of ϵ_d from one site to the next is determined by the Pd coordination number N —the smaller the coordination number, the higher in energy the d band. The step sites therefore bond most strongly and the terrace sites at the bottom of the steps bond most weakly. In Fig. 2(b) it can be seen that Pd atoms coordinated to an adsorbed NO molecule have an additional down-shift of ϵ_d . The NO-NO coupling is therefore also largely related to the d -band shift. The stability of the second NO molecule in site IV is higher when the first NO molecule is moved from site II to site I, because in the latter site the NO does not coordinate to Pd atoms which also coordinate to site IV.

In summary, we have presented density-functional theory results for NO bonding at Pd(211). The site occupation is observed to be nonsequential with an NO reorganization at higher coverage.

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